

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Docket No: Q93069

Toshihiko OKAMOTO, et al.

Appln. No.: 10/ 568,616 Group Art Unit: 1796

Filed : February 16, 2006 Examiner: Olatunde S. OJURONGBE

Title : CURING COMPOSITION WITH IMPROVED HEAT RESISTANCE

DECLARATION UNDER RULE 132

Honorable Commissioner of Patents and Trademarks,
Alexandria, Virginia 22313-1450

Sir:

I, Toshihiko Okamoto, a citizen of Japan and having postal mailing address of 1-19-19, Nonoue, Akashi, Hyogo 673-0017, Japan, declare and say that:

In March 1994, I was graduated from Graduate School of Engineering, Osaka University, and received a master's degree in the field of chemistry;

Since April 1994, I have been employed by Kaneka Corporation and engaged in the work of research and development of silyl terminated polyether sealants in High Performance Polymers Division;

I am the inventor of the above-identified application and am familiar with the technical field of the present invention;

I respectfully submit herewith my exact report;

In order to demonstrate the effect of the selective inventions according to the claims of the present application, I have carried out the following experiments.

Object

The experiments are to evaluate the curability and the heat resistance of the curing compositions obtained, by the same methods as those of the present Examples, from combinations of various components (A) having different contents of a $-NR^1-C(=O)-$ group and various components (B) (tin carboxylate or carboxylic acid) in which "the carbon atom adjacent to the carbonyl group" is a quaternary carbon atom, a tertiary carbon atom or a secondary carbon atom.

Experiments

(Synthesis of components (a))

By use of a polyoxypropylene triol having a molecular weight of about 3,000 as an initiator and zinc hexacyanocobaltate-glyme complex as a catalyst, polymerization of propylene oxide was carried out to yield a hydroxy group-terminated polypropylene oxide having a number average molecular weight of about 26,000, which was then used for the production of an allyl group-terminated trifunctional polypropylene oxide by the same method as that of Synthesis Example 4 in the present application. The obtained allyl group-terminated polypropylene oxide was reacted with 1.3 parts by weight of trimethoxysilane in the same manner as that of Synthesis Example 4 to yield a polyoxypropylene polymer (A-5) containing on average 2.0 trimethoxysilyl groups per one molecule at the terminal.

100 g (20 mmol) of a polyoxypropylene diol having a hydroxyl equivalent of 0.36 mmol/g and a molecular weight of about 5,000 as measured with the end group analysis method and 5.6 g (22.5 mmol) of MDI (*4,4'*-diphenylmethane diisocyanate, manufactured by Wako Pure Chemical Industries, Ltd.) having an NCO/OH ratio of 1.25 were mixed under a nitrogen atmosphere and stirred at 90°C for

3 hours to give an NCO-terminated polyoxypropylene, to which was then added 1.6 g (9 mmol) of γ -aminopropyltrimethoxysilane (manufactured by Momentive Performance Materials Inc.) and stirred at 40°C for 1 hour to yield a trimethoxysilyl group-terminated polyoxypropylene polymer (A-6). On the basis of the measurements by $^1\text{H-NMR}$ and GPC, it was found that the number of the groups represented by the general formula (1): $-\text{NR}^1-\text{C}(=\text{O})-$ is 4.8 per one molecule on average.

100 g (33 mmol) of a polyoxypropylene diol having a hydroxyl equivalent of 0.67 mmol/g and a molecular weight of about 3,000 as measured with the end group analysis method and 9.6 g (38.5 mmol) of MDI (4,4'-diphenylmethane diisocyanate, manufactured by Wako Pure Chemical Industries, Ltd.) having an NCO/OH ratio of 1.15 were mixed under a nitrogen atmosphere and stirred at 90°C for 3 hours to give an NCO-terminated polyoxypropylene, to which was then added 1.8 g (10 mmol) of γ -aminopropyltrimethoxysilane (manufactured by Momentive Performance Materials Inc.) and stirred at 40°C for 1 hour to yield a trimethoxysilyl group-terminated polyoxypropylene polymer (A-7). On the basis of the measurements by $^1\text{H-NMR}$ and GPC, it was found that the number of the $-\text{NR}^1-\text{C}(=\text{O})-$ groups is 7.7 per one molecule on average.

In the same manner as those of Examples 5-7 and Comparative Example 3 (see Table 2) in US 2006/0199933 A1 (i.e. the present application), the curability (tack-free time: TFT), the M50 value (50% tensile modulus) before heat curing and the retention rate of the M50 value after heat curing at 90°C for 14 days of the curing compositions set forth in the following table were measured. The results obtained are shown in the following table.

In the table below, the organic polymer (A-1) as

the component (A) refers to an organic polymer obtained by the method of Synthesis Example 1 in the present application.

The amount of Neostann U-50 in Experiment No.1 and that of tin 2-ethylhexanoate in Experiment No.5 in the following table were adjusted so that they were the same in molar amounts. The amount of Versatic 10 in Experiment No.6, that of 2-ethylhexanoic acid in Experiment No.10 and that of oleic acid in Experiment No.11 were also adjusted so that they were the same in molar amounts.

Experiment Nos. 1, 6 and 12 in the following table, which correspond to Examples 5 and 7 and Comparative Example 3 in the present application respectively, were re-evaluated as supplementary experiments.

Results

By comparison between Experiment Nos. 1-4 and between Experiment Nos. 6-9 in the following table, it was found that the greater the average number of the $-\text{NR}^1\text{-C}(=\text{O})-$ groups per one molecule is, the less the heat resistance is.

By comparison between Experiment Nos. 1 and 5, it was also recognized that tin carboxylate salts in which the carbon atom (α -carbon) adjacent to the carbonyl carbon atom is a quaternary carbon atom had remarkable rapid curabilities. Furthermore, by comparison between Experiment Nos. 6, 10 and 11, it was recognized that carboxylic acids in which the carbon atom (α -carbon) adjacent to the carbonyl carbon atom is a quaternary carbon atom had remarkable rapid curabilities.

As above, it is clear that only a combination of a hydrolyzable Si group-containing organic polymer (A) in which the average number of the $-\text{NR}^1\text{-C}(=\text{O})-$ groups per one molecule is a particular number and a curing catalyst (B) having a particular structure can attain to "excellence

in heat resistance and rapid curability although a non-organotin catalyst is used", which is the object of the present application.

Table

Component (A)	Composition (part(s) by weight)												Experiment Nos.
	1	2	3	4	5	6	7	8	9	10	11	12	
Component (A)	A-1	2.0 ⁽¹⁾	100										
	A-5	0.0 ⁽¹⁾		100									
	A-6	4.8 ⁽¹⁾		100									
	A-7	7.7 ⁽¹⁾			100								
Filler	Hakuenka CCR	120	120	120	120	120	120	120	120	120	120	120	120
Titanium Oxide	Tipaque R-820	20	20	20	20	20	20	20	20	20	20	20	20
Plasticizer	DIDP	55	55	55	55	55	55	55	55	55	55	55	55
Antisagging agent	Disparlon #6500	2	2	2	2	2	2	2	2	2	2	2	2
Photo-stabilizer	Sanol LS-770	1	1	1	1	1	1	1	1	1	1	1	1
Ultraviolet absorber	Tinuvin 327	1	1	1	1	1	1	1	1	1	1	1	1
Antioxidant	Irganox 1010	1	1	1	1	1	1	1	1	1	1	1	1
Dehydrating agent	A-171	2	2	2	2	2	2	2	2	2	2	2	2
Adhesion-imparting agent	A-1120	3	3	3	3	3	3	3	3	3	3	3	3
Tin carboxylate salt	Neostann U-50 Tin 2-ethylhexanoate (2)	5	5	5	4.4								
Carboxylic acid	Versatic 10 2-Ethylhexanoic acid (3)					6	6	6	6	6	6	6	5
Oleic acid ⁽⁴⁾													9.9
Amine	Farmin 20D	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Organotin compound	STANN BL												0.1
Curability	Tack-free time	min	20	76	25	20	69	15	70	20	15	33	70
M50 value before heat curing	MPa	0.43	0.44	0.62	0.65	0.46	0.37	0.37	0.54	0.55	0.39	0.34	0.56
Retention rate of M50 value after heat curing at 90°C for 14 days	%	96	102	85	74	93	100	105	92	80	100	97	76

- (1) Average number of $-\text{NR}^1-\text{C}(=\text{O})-$ groups per one molecule of polymer
- (2) $[(\text{C}_4\text{H}_9)\text{CH}(\text{C}_2\text{H}_5)\text{COO}]_2\text{Sn}$
- (3) $(\text{C}_4\text{H}_9)\text{CH}(\text{C}_2\text{H}_5)\text{COOH}$
- (4) $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed this 14th day of May , 2009

Toshihiko Okamoto

Toshihiko Okamoto